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Process for the preparation of an aqueous polymer dispersion by mini-emulsion polymerisation

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PROCESS FOR THE PREPARATION OF AN AQUEOUS POLYMER DISPERSION BY
MINI-EMULSION POLYMERISATION

5 The present invention relates to a process for the preparation of an aqueous polymer dispersion by mini-emulsion polymerisation.

10 The preparation of aqueous polymer dispersions by the technique called mini-emulsion polymerisation is known since several years. Mini-emulsion polymerisation offers a number of advantages over conventional emulsion polymerisation, such as the possibility to encapsulate or even to incorporate hydrophobic components into the polymer during the polymerisation. In addition to the monomers, water and surfactant which are generally used during conventional emulsion polymerisations, mini-emulsion polymerisation requires the presence of an additional component which stabilises the small emulsion droplets formed during the mini-emulsion process and before and during the polymerisation processes. These additional components are usually hydrophobic components that have no or extremely low water solubility and a good miscibility with the monomer. WO 00/29451 and US 5,686,518 disclose a series of hydrophobic components that are suitable for the stabilisation of mini-emulsions. In addition to these hydrophobic components, the mini-emulsions described therein require also a surfactant such as sodium lauryl sulphate or other alkylsulphates, sodium dodecyl benzene sulphonate or other alkyl or aryl sulphonates, sodium stearate or other fatty acid salts, or polyvinyl alcohol, in order to stabilise the emulsion droplets before and during the polymerisation and the polymer particles obtained after polymerisation. When these aqueous polymer dispersions are used for coatings or film formation, the presence of these surfactants often causes defects, for example by migration or by clustering into hydrophilic "pockets". The presence of surfactants lowers certain properties of the resulting coatings or films, such as water sensitivity or may cause other problems like water whitening and efflorescence.

25 The present invention overcomes these problems by providing a process for the preparation of aqueous dispersions by mini-emulsion polymerisation where these surfactants can be omitted or where their level can be significantly lowered.

30 The present invention therefore concerns a process for the preparation of an aqueous polymer dispersion by mini-emulsion polymerisation comprising the steps of

(a) forming a mixture comprising water, at least one amphiphilic stabilising polymer having a number average molecular weight M_n of 800 to 100000 and an acid number of 50 to 400 mg KOH/g, at least one hydrophobic co-stabiliser and at least one α,β -ethylenically unsaturated monomer,

35 (b) subjecting the mixture formed in (a) to high stress techniques so as to form a mini-emulsion comprising stabilised droplets having an average diameter of 10 to

1000 nm and comprising the hydrophobic co-stabiliser and monomer, dispersed in an aqueous phase,

(c) polymerising the monomer within the droplets.

It was found that the use of an amphiphilic stabilising polymer as defined herein permits to prepare stable mini-emulsions without the need to add conventional surfactants, such as alkyl, aryl, alkylaryl and arylalkylsulphates and sulphonates.

The amphiphilic stabilising polymer used in the process according to the invention exhibits an adequate balance of hydrophobicity and hydrophilicity such that it is suited for the stabilisation of oil-in-water emulsions. It is in general a polymer derived of a combination of hydrophobic monomers and hydrophilic monomers incorporating acid functions or functions leading thereto.

The amphiphilic stabilising polymer is preferably a copolymer derived from addition polymerisation of one or more ethylenically unsaturated hydrophobic monomers such as styrene, (meth)acrylic esters, isobutylene and derivatives thereof, with one or more ethylenically unsaturated hydrophilic monomers such as carboxylic monomers (for example acrylic acid, methacrylic acid, itaconic acid), sulfonic acid monomers or their salts (for example styrenesulfonic acid and 2-acrylamido-2-methylpropane sulfonic acid), phosphate monomers (for example ethylene glycol methacrylate phosphate), phosphonate monomers (for example vinylphosphonic acid), anhydrides (for example maleic anhydride), the latter being optionally hydrolysed or modified by an alcohol or amine.

Other amphiphilic polymers suitable for being used in the process according to the invention are those derived from step polymerisation such as polyurethanes and polyesters containing pendant acid functions. Suitable polyurethane polymers are those obtained from a polyurethane prepolymer which is the reaction product of:

- (i) at least one polyisocyanate (such as isophorone diisocyanate, dicyclohexylmethane diisocyanate and tetramethylethylenediisocyanate),
- (ii) at least one organic compound containing at least two reactive groups which can react with isocyanates (such as polyester polyols, polyether polyols and polycarbonate polyols which have a number average molecular weight within the range of 400 to 5,000), and
- (iii) at least one alcohol or polyol which is capable to react with an isocyanate group and which contains additional functional groups which are susceptible to provide good dispersion in water and which provides an acid function.

Such an alcohol or polyol typically has functional groups such as anionic salt groups or similar precursors which may be subsequently converted to such anionic salt groups, such as carboxylic or sulfonic acid groups. The carboxylate salt groups incorporated into the isocyanate-terminated polyurethane prepolymers generally are derived from hydroxycarboxylic acids represented by the general formula

(HO) x R(COOH) y , wherein R represents a straight or branched hydrocarbon residue having 1 to 12 carbon atoms, and x and y independently are integers from 1 to 3. The most preferred hydroxycarboxylic acids are the α,α -dimethylolalkanoic acids, wherein $x=2$ and $y=1$ in the above general formula, such as for example, the 2,2-

5 dimethylolpropanoic acid.

The amphiphilic stabilising polymer is more preferably a copolymer derived of styrene and maleic anhydride or a copolymer derived of styrene, α -methyl styrene and acrylic acid.

10 The amphiphilic stabilising polymer used in the process according to the invention preferably has a solubility in the aqueous phase of the mini-emulsion of at least 10^{-2} g/l (as measured at 25 °C), more preferably of at least 10^{-1} g/l, and most preferably of at least 1 g/l.

The amphiphilic stabilising polymer used in the process according to the invention preferably has a M_n of 900 to 50000, more preferably of 1000 to 25000.

15 The amphiphilic stabilising polymer used in the process according to the invention preferably has an acid number of 100 to 350 mg KOH/g, more preferably in the range of 150 to 300 mg KOH/g. The acid number is defined as the amount of potassium hydroxide (expressed in milligram) needed to completely neutralise one gram of the polymer.

20 The quantity of amphiphilic stabilising polymer used in the process according to the invention is generally in the range of 0.5 to 15 % by weight relative to the total weight of α,β -ethylenically unsaturated monomers used. The quantity of amphiphilic stabilising polymer does preferably not exceed 8 %, more preferably not 5 %, by weight. Preferably, the quantity of amphiphilic stabilising polymer is at least 1 %, especially at least 2 % by weight relative to the total weight of α,β -ethylenically unsaturated monomers used.

25 Hydrophobic co-stabiliser as used in the process according to the invention is meant to designate a compound which is both highly water insoluble and highly soluble in the α,β -ethylenically unsaturated monomer(s). The hydrophobic co-stabiliser used in the process according to the invention generally has a solubility in water of less than $5 \cdot 10^{-5}$ g/l, preferably less than $5 \cdot 10^{-6}$ g/l (as measured at 25°C).

30 Suitable hydrophobic co-stabilisers are hydrocarbons, especially alkanes or cycloalkanes, containing at least 12 carbon atoms (e.g. hexadecane, octadecane), long chain alcohols (e.g. hexadecanol, octadecanol), halogenated hydrocarbons, organosilicon compounds, long-chain esters, oils such as vegetable oils (e.g. olive oil), hydrophobic dye molecules, capped isocyanates, and also oligomeric products of polymerisation, polycondensation or polyaddition. Also polymeric co-stabilisers have been described, for example in US 5,686,518.

According to a particular embodiment of the process according to the invention, a reactive hydrophobic co-stabiliser can also be used, alone or in addition to a non-reactive hydrophobic co-stabiliser. By reactive hydrophobic co-stabilisers are meant those co-stabilisers that participate in the subsequent polymerisation reaction.

- 5 Examples of such compounds are hydrophobic (co)monomers such as stearyl acrylate and other long chain (meth)acrylates, macromonomers; hydrophobic chain transfer agents such as dodecyl mercaptane, octadecyl mercaptane and other long chain mercaptanes; and or even hydrophobic initiators such as 2,5-dimethyl-2-5-di(2-ethylhexanoylperoxy) hexane and other long chain (hydro)peroxides or azo
10 initiators.

- The hydrophobic co-stabiliser used in the process according to the invention is preferably chosen from alkanes or alcohols containing from 12 to 24 carbon atoms, especially hexadecane, and from acrylates containing from 18 to 22 carbon atoms, and their mixtures. A mixture of acrylates is for example commercialised under the name
15 of Norsocryl™ A-18-22, (ATOFINA).

- The hydrophobic co-stabiliser is generally added in an amount of from 0.05 to 40% by weight, preferably from 0.1 to 10% by weight, and with particular preference from 0.2 to 5% by weight, based on the overall weight of the mixture prepared in step
20 (a) of the process according to the invention. In the special case wherein hydrophobic (co)monomers such as described here above are used that function both as hydrophobic co-stabiliser and as α,β -ethylenically unsaturated monomer, the quantity of such hydrophobic (co)monomer can be as high as 70 % by weight based on the overall weight prepared in step (a).

- When the hydrophobic co-stabiliser is not a (co)monomer, the hydrophobic co-stabiliser is preferably added in an amount of from 0.1 to 10% by weight, more preferably from 0.2 to 8 % by weight, and with particular preference from 0.5 to 5% by weight, based on the overall weight of monomer(s).

- The α,β -ethylenically unsaturated monomers which can be used in the process according to the invention are those which have a low solubility in water. In general
30 the α,β -ethylenically unsaturated monomer has a solubility in water of not more than 15 %, preferably not more than 5 %, and most preferably not more than 3%. Solubilities of these monomers are as measured at 25°C and denote grams of dissolved monomer per 100 grams of water.

- Suitable α,β -ethylenically unsaturated monomers are alkyl acrylates or alkyl
35 methacrylates (e.g. methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, isobornyl methacrylate, and lauryl methacrylate), polymerizable aromatic compounds (for example styrene, α -methyl styrene, vinyl toluene and t-butyl styrene), polymerizable nitriles (for example

acrylonitrile and methacrylonitrile), polymerizable amide compounds, α -olefin compounds such as ethylene, vinyl compounds such as vinyl acetate, vinyl propionate, and longer chain vinyl ester homologues; vinyl ethers, vinyl and vinylidene halides, diene compounds such as butadiene and isoprene. Other suitable α, β -ethylenically unsaturated monomers are those with fluorine or silicon atoms, such as 1H, 1H, 5H-octafluoropentyl acrylate, and trimethylsiloxyethyl acrylate. Preferably α, β -ethylenically unsaturated monomers are chosen from styrenes, acrylates, methacrylates, vinyl and vinylidene halides, dienes, vinyl esters and their mixtures. Particularly preferred are methyl methacrylate, styrene, vinyl acetate, methyl acrylate, butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, butadiene and vinyl chloride.

The quantity of α, β -ethylenically unsaturated monomers used in the process according to the invention is in general from 10% to 70%, preferably from 18% to 60%, by weight based on the total weight of mixture (a).

According to another embodiment of the process according to the present invention, one or more water-soluble monomers (hereafter designated as secondary monomers) may be added to the mixture formed during step (a) in addition to the α, β -ethylenically unsaturated monomer(s). These secondary monomers are generally addition polymerizable ethylenically unsaturated organic compounds which have a water solubility higher than 15 % and are used only in small percentages in a monomer mix and only in the presence of at least one α, β -ethylenically unsaturated monomer such as described here above. The percentage of secondary monomer present in the monomer mix does preferably not exceed 6 %, is more preferably 0 to 4 %, and most preferably 0 to 2 %, based on the total monomer weight. Examples of secondary monomers are acrylic acid, methacrylic acid, 2-sulfoethyl methacrylate, and maleic anhydride. The use of secondary monomers may impart desired properties to the coatings produced when using the polymer dispersions obtained by the process according to this invention.

In another embodiment of the process according to the invention, at least one surfactant chosen from anionic, cationic and non-ionic surfactants is added to the mixture formed in step (a). Suitable surfactants include alkyl sulphates, such as sodium lauryl sulphate; alkyl, aryl, alkylaryl and arylalkyl sulphonates, such as sodium dodecyl benzene sulphonate; fatty acid salts such as sodium stearate; polyvinyl alcohol, fatty alcohol polyglycol ethers, such as ethoxylated linear fatty alcohols containing from 10 to 100 ethylene oxide units.

The amount of surfactant generally does not exceed 2 % by weight, based on the total weight of monomers used in the process according to the invention. Preferably, the amount of surfactant does not exceed 1% by weight, and even more preferred, the amount of surfactant does not exceed 0.5% by weight based on monomer.

The mixture formed in step (a) may also contain one or more components that modify the pH. Especially when the stabilising amphiphilic polymer contains carboxylic acid functions, it may be necessary to prepare and to polymerise the mini-emulsion at an elevated pH for the stabilising polymer to exhibit proper amphiphilicity. In that case, a suitable pH range is 6.0 to 10.0, depending on the nature of the other components in the polymer. A further preferred pH range is 7.5 to 10.0. When the stabilising polymer contains acid functions derived from sulfonic acid, sulphate, phosphate or phosphonate, a suitable range of pH is 2.0 to 10.0. Compounds capable of adjusting pH are ammonia, amines (for example triethyl amine, triethanol amine, dimethylamino hydroxypropane), carbonate salts (for example sodium carbonate), bicarbonate salts (for example sodium bicarbonate), hydroxides (for example sodium hydroxide) or oxides (for example calcium oxide). The pH-adjusting compound is preferably chosen from ammonia or sodium hydroxide.

The pH-adjusting compound may be added during step (a). Preferably the pH-adjusting compound is added to the stabilising amphiphilic polymer before the latter is used in step (a).

The formation of the mixture in step (a) of the process according to the invention is preferably done by mixing a premixture (i) comprising the amphiphilic stabilising polymer and water with a premixture (ii) comprising the hydrophobic co-stabiliser and the α,β -ethylenically unsaturated monomer(s).

The premixture (i) is generally prepared by adding the amphiphilic stabilising polymer to water, preferably at a temperature of 0 to 100 °C. To this premixture (i) may optionally be added, one or more surfactants as described here above, one or more secondary water soluble monomers as described here above, a pH adjusting compound and/or a polymerisation initiator.

When an amphiphilic stabilising polymer containing carboxylic acid functions is used in the process according to the invention, it is preferred to prepare a premixture (i) comprising a pH-adjusting compound such as described here above so that the solubility of the amphiphilic stabilising polymer in this premixture (i) becomes at least 10⁻² g/l (as measured at 25 °C), more preferably at least 10⁻¹ g/l, and most preferably at least 1 g/l. In this case, it is particularly preferred to add this pH-adjusting compound to the amphiphilic polymer before adding thereto water, and, optionally, the other components of the premixture (i).

The premixture (ii) is generally prepared by adding the desired amount of hydrophobic co-stabiliser to the α,β -ethylenically unsaturated monomer(s), preferably under gentle agitation. This premixture is generally prepared at room temperature, preferably until a clear solution is obtained. To this premixture (ii) may optionally be added one or more secondary water-soluble monomers as described here above and/or a polymerisation initiator.

The formation of the mixture during step (a) of the process according to the invention is generally done at a temperature of 0 to 100 °C, preferably at room temperature.

The mixture obtained under step (a) is then submitted, in step (b) of the process according to the invention, to high stress techniques so as to form a mini-emulsion comprising stabilised droplets having a average diameter of 10 to 1000 nm. The term "mini-emulsion" used herein denotes a monomer emulsion in which the average droplet diameter is from 10 to 1000 nm. This term is used to distinguish conventional monomer emulsions and emulsion polymerisation processes, wherein the size of the droplets or micelles is larger, in general from about 1 to 10 µm.

The droplet diameter is measured by using dynamic light scattering, for example on a Coulter™ N4 Plus or a Nicomp 380 ZLS device. The sample preparation involves dilution of a mini-emulsion sample by deionized water or, preferably, by deionized water which is saturated with the monomer(s) that is present in the mini-emulsion. Droplet size is determined directly after sample preparation, in all cases within 15 minutes.

Step (b) of the process according to the invention is preferably conducted as to obtain a mini-emulsion in which the droplets have an average diameter not exceeding 500 nm, more preferably not exceeding 400 nm, even more preferably not exceeding 300 nm. Step (b) is preferably conducted as to obtain a mini-emulsion in which the droplets have an average diameter of at least 80 nm.

In step (b) the mixture is subjected to high stress techniques. Stress is described as force per unit area. One manner in which stress is exerted is by shear. Shear means that the force is such that one layer or plane moves parallel to an adjacent one. Stress can also be exerted from all sides as a bulk, compression stress, such that stress is exerted without almost any shear. Another manner of exerting stress is by cavitation, which occurs when the pressure within a liquid is reduced enough to cause vaporisation. The formation and collapse of the vapour bubbles occurs violently over a short time period and produces intense stress. Another manner of applying stress is the use of ultrasonic energy.

In step (b) of the process according to the invention, it is preferred to use an equipment capable of producing localised high shear, preferably along with moderate bulk mixing. More preferably high shear mixing is obtained by using ultrasound treatment, colloid mill and/or homogenizer.

The temperature used during step (b) of the process according to the invention is, in general, any temperature between the freezing point and the boiling point of the mixture and the components present therein. Preferred temperatures for monomer mini-emulsion formation are from 20 to 50° C., more preferentially from about 25 to 40 °C.

Step (b) results in the formation of an essentially stable mini-emulsion which comprises an aqueous continuous phase and droplets comprising the α,β -ethylenically unsaturated monomer or monomers and the hydrophobic co-stabiliser; these droplets also noted as the disperse phase. Substantially all or at least a major part of the amphiphilic stabilising polymer is thought to be located at or near the interface between the droplets and the aqueous medium. The solubility of the stabilising polymer in the monomer, when the stabilising polymer is in the deprotonated state is usually below 2%, preferably below 1%, by weight based on monomer weight.

By mini-emulsion which is essentially stable is meant to designate that its shelf life is sufficiently long so that the monomer content of the emulsion can be polymerised in less time than the time required for phase separation. The mini-emulsions obtained by the process of the invention generally present a shelf life of more than 24 hrs. even more than several days.

In step (c) of the process according to the invention, the monomer(s) within the droplets is polymerised. The monomer(s) is generally polymerised under free radical polymerisation conditions, preferably in the presence of a free radical initiator. The polymerisation initiator may be either a water-soluble or an oil soluble compound. Suitable free radical initiators are known in the art. These include, for example, organic peroxides such as benzoyl peroxide, lauroyl peroxide, 2,5-dimethyl 2,5-di(2-ethylhexanoylperoxy) hexane and dicumyl peroxide; inorganic persulphates such as potassium persulphate or ammonium persulphate; and azo initiators such as azobis(isobutyronitrile) (AIBN) and azobis(1-cyclohexanecarbonitrile); and redox pairs such as $\text{Fe}^{2+}/\text{H}_2\text{O}_2$; $\text{ROH}/\text{Ce}^{4+}$ (where R is an organic group such as C1-C6 alkyl or C5-C8 aryl) and $\text{K}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$.

The free-radical initiator may be added to the mini-emulsion obtained after step (b), before step (b) and/or during step (b). The free-radical initiator is preferably added to premixture (ii) which is used in step (a) of the process according to the invention in those cases where the solubility of the initiator in the premixture (ii) is higher than in the premixture (i). In those cases where the solubility of the initiator in premixture (i) is higher than in premixture (ii), the initiator can be added to the mixture formed in step (a) or during or after step (b) of the process according to the invention. In that case, it is preferably added to the mini-emulsion obtained after step (b).

During step (c) of the process according to the invention, it may be necessary to add a pH adjusting compound such as described in relation to step (a), in order to retain the stabilising polymer in an amphiphilic state. This is in particular the case when the pH drops during the reaction. This may be induced by the dissociation of persulphate initiators (for example ammonium persulphate) or by the evaporation of

the pH adjusting compound present in the mixture formed in step (a) (for example when ammonia is used). The pH-adjusting compound added during step (c) may be the same or different from the one added during step (a).

5 The polymerisation in step (c) may be carried out over a broad temperature range, generally from about 20 to 90 °C. The preferred polymerisation temperature depends on the choice of initiator. A preferred polymerisation temperature range is from about 25 to 80 °C.

The polymerisation in step (c) of the process according to the invention is usually conducted for 10 min to 24 hrs.

10 The aqueous polymer dispersion obtained after step (c) of the process according to the invention contains generally polymer particles having an average diameter in the range of about 10 to about 1000 nanometers. The aqueous polymer dispersion, which is also often called polymer emulsion or latex, preferably contains polymer particles having an average diameter in the range from 80 to 400 nanometers.

15 Polymer latexes obtained by the process according to the invention presents the advantage of having a improved runnability. The polymer latexes obtained by the process according to the invention have a good stability, generally exceeding 6 months or even more.

20 Polymer latexes obtained by the process according to the invention are useful for the same kind of purposes as polymer latexes already known in the art. They are especially suitable for the preparation of decorative and protective coatings or films, pressure sensitive adhesives, inks, glues, stains, varnishes, constructive adhesives. The coatings or films obtained from the polymer latexes obtained by the process according to the invention generally have an improved water resistance and a lower
25 water absorption. They also present less water whitening, an improved gloss, a better blocking resistance and a higher film hardness.

The following examples are submitted for a better understanding of the invention without being restricted thereto.

EXAMPLES

30 Example 1:

1.1 Preparation of aqueous solution of amphiphilic stabilising polymer :

60 g of a copolymer of styrene, d-methyl styrene and acrylic acid having a Mn of 6500 and an acid number in the range of 193 to 215 (Morez™101 resin, commercialised by Rohm & Haas) was added to a mixture of 17.9 g ammonia (25%
35 w/w) and 125 g demineralised water while stirring. The solution was then heated to 70°C and left to stir until the Morez resin was completely dissolved. The resulting solution had 29.7% (w/w) solids.

1.2 Preparation of organic solution containing hydrophobic co-stabiliser and α,β -ethylenically unsaturated monomer:

10

0.29 g of hexadecane was dissolved in 14.4 g of styrene.

1.3 Preparation of a mixture :

2.28 g of the aqueous solution prepared in 1.1 was mixed with 57.6 g demineralized water. Then, the organic solution of hexadecane in styrene prepared in 1.2 was added to this aqueous solution while stirring (using a magnetic stirring bar at 1000 rpm). The stirring of this mixture was continued for 10 minutes.

1.4 Preparation of a mini-emulsion :

The resulting mixture obtained in 1.3 was then subjected to ultrasound treatment using a Branson Sonifier 450 (output control at 8 and a duty cycle of 90%) for 5 minutes. The resulting mini-emulsion had a droplet size of approximately 191 nm.

1.5 Polymerisation :

0.07 g of potassium persulphate was dissolved in the mini-emulsion obtained in 1.4, which was then transferred to a sealed glass bottle and polymerised for 6 hours at 70 °C by controlling the temperature with a water bath.

The resulting polymer dispersion had a particle size of 176 nm and contained only 1.4% coagulum.

Example 2

Example 1 was repeated except that the sonication time of 5 minutes instead of 10 minutes.

The mini-emulsion had a droplet size of approximately 416 nm and the resulting polymer dispersion had a particle size of 124 nm. 7.6% of the polymer was coagulated.

Example 3

3.1 Preparation of solution of amphiphilic stabilising polymer :

80 g of styrene-maleic anhydride copolymer having an acid number in the range of 165 to 205 (SMA1440 commercialised by Akofina) was added to a mixture of 21 g ammonia (25% w/w) and 400g demineralised water while stirring. The solution was then heated to 70°C and left to stir until the SMA resin was largely dissolved. 100 g demineralised water was added. The aqueous solution was decanted from undissolved SMA resin to give a solution of 8.3% (w/w) solids.

3.2 Preparation of the organic mixture containing hydrophobic co-stabiliser and α,β -ethylenically unsaturated monomer :

200.2 g of methyl methacrylate, 85.8 g of butyl acrylate and 5.72 g of hexadecane were mixed together under gentle stirring. 2.86 g of 1,1'-azobis(1-cyclohexanecarbonitrile) (V40, Wako) was additionally dissolved in this mixture.

3.3 Preparation of the mixture :

636 g of demineralised water and 0.44g of a non-ionic surfactant mixture of ethoxylated linear fatty alcohols (Disponitma 3065 commercialised by Cognis) were joined together in 1.2L beaker. 68.9 g of the SMA solution such as prepared in 3.1 was added to this water/surfactant mixture.

Under stirring, the organic mixture as prepared in 3.2 was added slowly to the aqueous medium. The mixture was kept stirring for 30 minutes.

3.4 Preparation of a mini-emulsion :

The mixture obtained in 3.3 was subjected to high shear using a 400W, Dr. Hielscher UP4005 sonicator probe while magnetic stirring was continued to achieve bulk mixing. The amplitude setting of the device was set to 60% at a duty cycle of 0.9. Sonication lasted for 10 minutes. During the sonification process, the beaker containing the mixture was kept in a water bath to keep the temperature of the mixture cool.

A mini-emulsion was obtained.

3.5 Polymerisation :

The mini-emulsion obtained in 3.4 was transferred to a polymerisation set-up consisting of a 1 l double jacketed glass reactor connected to a water bath and equipped with a mechanical anchor stirrer. The temperature of the water bath was set at 70°C. The mini-emulsion was heated for 4 hrs. after which it was cooled and filtered. The resulting polymer dispersion contained 28.5% of solids and had a particle size of 195 nm.

Example 4

4.1 Preparation of aqueous solution of amphiphilic stabilising polymer :

60 g of a copolymer of styrene, α -methyl styrene and acrylic acid having an Mn of 1200 and an acid number of 235 (Morez™300 resin, commercialised by Rohm & Haas) was added to a mixture of 20.5 g ammonia (25% w/w) and 125 g demineralised water while stirring. The solution was then heated to 70°C and left to stir until the Morez resin was completely dissolved. The resulting solution had 29.3% (w/w) solids.

4.2 Preparation of a mini-emulsion

When example 1.2 to 1.5 is repeated using the solution of Morez300 prepared under 4.1 here above (instead of 1.1), a polymer dispersion is obtained with a particle size of 163 nm and 1.3% coagulum. The droplet size of the mini-emulsion before polymerisation was approximately 177 nm.

Example 5

1.97g of the resin solution prepared in example 1.1 was mixed with 44.2g water. Then a solution containing 0.59 g hexadecane and 0.59g of 2,5-dimethyl 2,5-di(2-ethylhexanoylperoxy) hexane (Luperox™256 of Atofina) dissolved in 29.6 g butyl acrylate was added thereto while being stirred using a magnetic stirring bar. After 10 minutes, the resulting mixture was subjected to ultrasound using a Branson Sonifier 450 (output control at 8 and a duty cycle of 80%) for 5 minutes. During the sonification process, the beaker containing the emulsion was cooled in an ice bath.

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The resulting mini-emulsion (droplet size approximately 165 nm) was transferred to a sealed glass bottle and submerged in a water bath of 70°C for 6 hours. The polymer dispersion thus obtained had a particle size of 310 nm and a solids content of 39.7% (w/w) and low coagulum.

5 Example 6:

6.1 Preparation of organic solution containing hydrophobic co-stabiliser and α,β -ethylenically unsaturated monomer :

0.31 g of hexadecane was dissolved in 14.4 g of butyl acrylate.

6.2 Preparation of a mixture :

10 2.28 g of the aqueous solution prepared in Example 1.1 was mixed with 57.6 g demineralized water.

Then, the organic solution of hexadecane in butyl acrylate prepared in 6.1 was added to this aqueous solution while stirring (using a magnetic stirring bar at 1000 rpm). The stirring of this mixture was continued for 10 minutes.

15 6.3 Preparation of a mini-emulsion :

The resulting mixture obtained in 6.2 was then subjected to ultrasound treatment using a 400W, Dr. Hielscher UP400S sonicator probe while magnetic stirring was continued to achieve bulk mixing. The amplitude setting of the device was set to 90% and the duty cycle to 0.8. Sonication lasted for 10 minutes..

20 6.4 Polymerisation :

0.07 g of ammonium persulphate was dissolved in the mini-emulsion obtained in 6.3, which was then transferred to a 100ml three-necked glass reactor, equipped with a reflux condensor. The reactor was heated using an oil bath. Polymerisation lasted for 6 hours at 70 °C. The resulting polymer dispersion had a particle size of 134 nm and contained only 0.5% coagulum.

25 Comparative example 7 (not according to the invention):

Example 6 was repeated without subjecting the mixture formed in 6.2 to sonification. The resulting polymer dispersion had 3.3% coagulum and a particle size of 930nm. The polymer dispersion was unstable as witnessed by partial phase separation after 24hrs. of storage.

30 separation after 24hrs. of storage.

Example 8

2.4 g of the resin solution which was prepared in example 1.1 was added to 35.1 g of demineralised water.

35 0.72 g of hexadecane and 0.72 g of 2,5-dimethyl 2,5-di(2-ethylhexanoylperoxy) hexane (Luperox™256, Atofina) were dissolved in 36.1 g methyl methacrylate monomer.

This monomer solution was added to the aqueous medium under stirring.

After 10 minutes of stirring, the resulting mixture was subjected to ultrasound using a Branson Sonifier 450 (output control at 8 and a duty cycle of 80%) for 10 minutes.

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During the ultrasonification, the beaker containing the mixture was kept in an ice bath to keep temperature low and prevent polymerisation.

The resulting mini-emulsion had a average droplet diameter of 128 nm.

5 The mini-emulsion was transferred into a glass bottle which was submerged in a water bath of 70°C for 6 hours.

The resulting polymer dispersion had an average particle diameter of 245 nm and was of 49.8% solids. The amount of coagulum was negligible.

Example 9

10 68.9g of the resin solution prepared in example 3.1 and 10g of a 5% solution of sodium hydroxide in water were added to 275g of demineralised water.

5.7 g of a mixture of C18-C22 acrylates (NoracrylTMA-18-22 commercialised by Atofina) were dissolved in a mixture of 96g methyl methacrylate and 41g butyl acrylate.

15 The monomer mixture was added to the aqueous medium while stirring. After 10 minutes of stirring, the mixture was subjected high shear using a 400W, Dr. Hielscher UP400S sonicator probe while magnetic stirring was continued to achieve bulk mixing. The amplitude setting of the device was set to 60% at a duty cycle of 0.9. Sonication lasted for 10 minutes.

20 The mini-emulsion was transferred to a polymerisation set-up consisting of a 1L double jacketed glass reactor connected to a water bath and equipped with a mechanical anchor stirrer. 0.8g of ammonium persulphate was added to the mini-emulsion.

The temperature of the water bath was set at 70°C. The mini-emulsion was heated for 6 hrs. after which it was cooled and filtered. The resulting polymer dispersion
25 contained 28.4% of solids and had a average particle size of 123 nm.

Samples taken after 2 and 4 hrs had average particle diameters of 114 and 119 nm respectively.

14

CLAIMS

1. Process for the preparation of an aqueous polymer dispersion by mini-emulsion polymerisation comprising the steps of
 - 5 (a) forming a mixture comprising water, at least one amphiphilic stabilising polymer having a number average molecular weight M_n of 800 to 100000 and an acid number of 50 to 400 mg KOH/g, at least one hydrophobic co-stabiliser and at least one α,β -ethylenically unsaturated monomer ;
 - 10 (b) subjecting the mixture formed in (a) to high stress techniques so as to form a mini-emulsion comprising stabilised droplets having an average diameter of 10 to 1000 nm and comprising hydrophobic co-stabiliser and monomer, dispersed in an aqueous phase ;
 - (c) polymerising the monomer within the droplets.
2. Process according to claim 1, wherein the amphiphilic stabilising polymer is a
15 polymer derived of a combination of hydrophobic monomers and hydrophilic monomers incorporating acid functions or functions leading thereto.
3. Process according to claim 2, wherein the amphiphilic stabilising polymer is a copolymer derived of styrene and maleic anhydride or a copolymer derived of styrene, α -methyl styrene and acrylic acid.
- 20 4. Process according to any of claims 1 to 3, wherein the amphiphilic stabilising polymer has a solubility in the aqueous phase of at least 10^{-2} g/l.
5. Process according to any of claims 1 to 4, wherein the quantity of amphiphilic stabilising polymer used is in the range of 0.5 to 15 % by weight relative to the total weight of α,β -ethylenically unsaturated monomer.
- 25 6. Process according to any of claims 1 to 5, wherein the hydrophobic co-stabiliser has a solubility in water of less than $5 \cdot 10^{-5}$ g/l.
7. Process according to any of claims 1 to 6, wherein the hydrophobic co-stabiliser is chosen from alkanes or alcohols containing from 12 to 24 carbon atoms and from acrylates containing from 18 to 22 carbon atoms, and their mixtures.
- 30 8. Process according to any of claims 1 to 7, wherein the hydrophobic co-stabiliser is used in an amount of from 0.05 to 40% by weight based on the overall weight of the mixture prepared in step (a).
9. Process according to any of claims 1 to 8, wherein the α,β -ethylenically unsaturated monomer has a solubility in water of not more than 15 %.
- 35 10. Process according to any of claims 1 to 9, wherein the α,β -ethylenically unsaturated monomer is chosen from styrenes, acrylates, methacrylates, vinyl and vinylidene halides, dienes, vinyl esters and their mixtures.

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11. Process according to any of claims 1 to 10, wherein not more than 6 % by weight based on the total monomer weight of one or more water-soluble monomer having a water solubility higher than 15 % is added to the mixture of step (a).
12. Process according to any of claims 1 to 11, wherein not more than 2 % by weight, based on the total weight of monomers, of a surfactant chosen from anionic, cationic and non-ionic surfactants is added to the mixture formed in step (a).
13. Process according to any of claims 1 to 12, wherein one or more components that modify the pH are added to the mixture formed in step (a).
14. Process according to any of claims 1 to 13, wherein step (b) is conducted so as to form a mini-emulsion comprising stabilised droplets having an average diameter of at least 80 nm and not exceeding 500 nm.
15. Process according to any of claims 1 to 14, wherein the high stress technique of step (b) is applied by an equipment capable of producing localised high shear, preferably along with moderate bulk mixing.
16. Process according to any of claims 1 to 15, wherein the monomer within the droplets is polymerised in the presence of a free radical initiator.

1

ABSTRACT

The invention relates to a process for the preparation of an aqueous polymer dispersion by mini-emulsion polymerisation comprising the steps of (a) forming a mixture comprising water, at least one amphiphilic stabilising polymer having a number average molecular weight M_n of 800 to 100000 and an acid number of 50 to 400 mg KOH/g, at least one hydrophobic co-stabiliser and at least one α,β -ethylenically unsaturated monomer : (b) subjecting this mixture to high stress techniques so as to form a mini-emulsion comprising stabilised and polymerising the monomer within the droplets.

PCT Application

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